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Effects of As Doping on Properties of ZnO Films

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ABSTRACT

A series of ZnO thin films with various deposition temperatures were prepared on (100) GaAs substrates by radio-frequency magnetron sputtering using ZnO target. The ZnO films were studied by field emission scanning electron microscope(FESEM), x-ray diffraction(XRD), photoluminescence(PL), cathodoluminescence(CL), and Hall measurements. The structural, optical, and electrical properties of the films were discussed as a function of the deposition temperature. With increasing temperature, the compressive stress in the films was released and their crystalline and optical properties were improved. From the depth profile of As measured by secondary ion mass spectrometry(SIMS), As doping was confirmed, and, in order to activate As dopant atoms, post-annealing treatment was performed. After annealing treatment, electrical and optical properties of the films were changed.

INTRODUCTION

Recently, zinc oxide (ZnO) has been emerged as an attractive material for application to the optical devices such as blue-, violet-, and UV-light emitting diodes(LEDs) and laser diodes(LDs) [1]. ZnO has very strong spontaneous emissions from bound excitons even at room temperature due to the large exciton binding energy of ~60 meV, as well as has structural and optical properties similar to GaN widely used to optical devices in present. Also, ZnO has high cohesive energy and melting temperature due to the high Zn-O bond strength, resulting in high-temperature stability during process [2,3].

For development of optical devices based on ZnO, GaAs can be used as a useful substrate material and it is attributed to the possibility of high level of monolithic system through the integration of optical components[4]. In addition, GaAs can be used as a p-type dopant source in ZnO film, which is essential to application of ZnO for optoelectronic devices [5]. However, because of the problems related to thermal stability and stress due to large lattice mismatch of about 19 % between ZnO and GaAs, a few studies of ZnO thin film on GaAs have been reported [6-9]. In general, it has known that thin films composed of polycrystalline structures are difficult to apply for optical devices due to the poor optical property originated from defect-related deep-level emissions[10].

In this study, we report on the effects of deposition temperature on properties of ZnO thin films prepared on GaAs (100) by rf magnetron sputtering. Then, effects of post-annealing treatment for ZnO films were discussed through Hall and PL measurements.

EXPERIMENTAL DETAILS

ZnO films were deposited by radio frequency(rf) magnetron sputtering. A 2-in. diameter and 5-N purity ZnO target were used to deposit the films. The substrates used were semi-

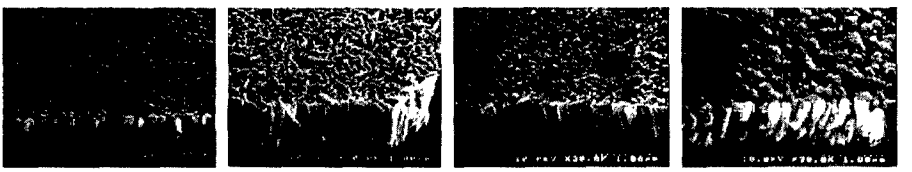
insulating (100) GaAs wafers. The sputtering chamber was evacuated to 2×10^{-6} Torr before sputtering. The ambient gases used were the mixed Ar and O_2(1:1) and the working pressure was fixed at 1×10^{-2} Torr. In order to investigate the effects of the deposition temperature on the properties of ZnO film, a series of films prepared at different temperatures between room temperature(R.T.) and 450 ℃. The thicknesses measured by α-step were in the ranges of 0.7 ~ 1 ㎛. After deposition, the surface morphology of the films was monitored by field emission scanning electron microscope (FESEM), and the crystallinity of the films was investigated by X-ray diffraction (XRD). To investigate the optical properties of ZnO films, photoluminescence (PL) and cathodoluminescence (CL) measurements were performed at R.T. In PL measurements, an excitation source was Ar laser with a wavelength of 352 nm and a power of 100 mW. The electrical properties of the ZnO films were determined by Van der Paw Hall measurements. For the films deposited at 350 and 450 ℃, post-annealing treatment was performed at 500 ℃ for 2 hours in vacuum to activate As dopants, and their electrical and optical properties were investigated by Hall and PL measurements.

DISCUSSION

Figure 1 shows FESEM images from ZnO films deposited at different temperatures. The images showed all films consist of columnar grains perpendicular to substrates. It was clearly observed that the shape of the grains changed from needle to hexagonal and, as deposition temperature increased, the grain size of the films became larger due to the grain growth.

Figure 2 shows the root-mean-square(rms) roughness as a function of deposition temperature measured by atomic force microscope(AFM) in the 5×5 ㎛^{2} area. It was observed that the rms roughness increased with increasing temperature, and it is attributed that the film surface became rough due to grain growth as shown in Fig.1. This fact indicates that deposition temperature significantly affects on the surface morphology of the films.

Figure 3 shows θ-2θ XRD patterns of ZnO films deposited at different deposition temperatures (T_D). The peak intensities and dominant peak position were varied as different T_D. It is notable that ZnO films deposited at room temperature were predominantly deposited along (0002) direction and the peak intensity was relatively strong compared to the films deposited at 250 ℃ and 350 ℃, and its position was shifted toward the lower-angle side than that of ZnO film deposited at 450 ℃. The diffraction from $(10\bar{1}1)$ plane was dominant for the films deposited at 250 ℃, whereas, as deposition temperature increases, the diffraction from (0002) plane became dominant. The c-axis lattices constant of the ZnO calculated from Bragg



(a) R.T. (b) 250 ℃ (c) 350 ℃ (d) 450 ℃

Figure 1. SEM image of the ZnO films deposited at different temperatures

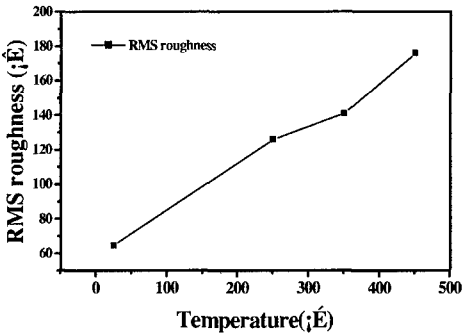


Figure 2. rms roughness of ZnO films as a function of deposition temperature.

condition for the (0002) plane are 5.226 Å for the film deposited at room temperature and 5.208 Å for 450 ℃. Compared with the lattice constant of a bulk single crystal ZnO, 5.207 Å, it can be explained that the film deposited at room temperature is under compressive stress, but the stress of the film was almost relaxed for the film deposited at 450 ℃ [13].

In order to study the optical properties of the ZnO films, photoluminescence(PL) measurements were performed at room temperature, and the results are shown in Figure 4. It was observed that all films, except the film deposited at room temperature, showed both the near band-edge emission(NBE) at ~3.26 eV and the deep-level emission around ~2.9 eV. It is known that the near band-edge emission corresponds to the recombination of excitons bound to donors. However, the origin of the deep-level emission is not clearly understood yet. It might be attributed to both native defects like oxygen vacancies and impurities unintentionally introduced during the film deposition[14,15]. With increasing deposition temperature, intensity of the band-edge emission was increased, and the PL intensity ratio of NBE emission to the defect level emission was ~8. Considering that the epitaxial ZnO films grown by MOCVD have the ratio less than 1 and the films grown by MBE have 5~20 [15,16]. It is thought that the films in this study have relatively low defect levels.

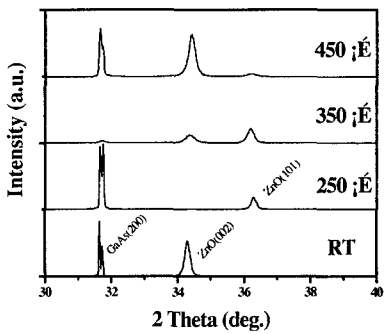


Figure 3. XRD patterns of the films with different deposition temperatures.

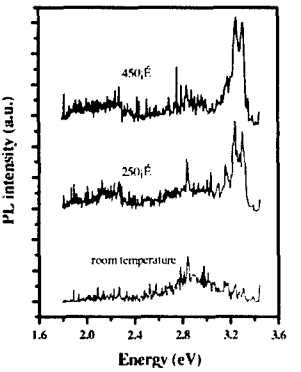


Figure 4. PL spectra of the ZnO films deposited at different temperatures.

Cathodoluminescence (CL) measurements were also performed to investigate further optical properties of the films. Figure 5 shows the CL spectra of the ZnO films deposited at room temperature and 450 ℃. The films deposited at room temperature exhibited the visible emission peak located at 2.0 eV without band-edge emission. On the other hand, a strong near band-edge emission at 3.28 eV was observed at 450 ℃. The emission at 2.0 eV was associated with defect level in ZnO films. However, the observation of a strong NBE for the films deposited at 450 ℃ implies that they are optically high-quality.

In order to investigate the dopant distribution in the films, SIMS analysis was carried for the films deposited at 350 ℃ and 450 ℃, and the results are shown in Figure 6. The plots show that the considerable amounts of As and Ga atoms are diffused into the as-grown ZnO films from GaAs substrates. As deposition temperature increased from 350 to 450 ℃, the concentrations of these atoms were increased due to the increase of vapor pressure. Vapor pressure of Ga is much lower than that of As below 500℃, and this caused the difference of doping concentration between Ga and As atoms. It is notable that these impurities are

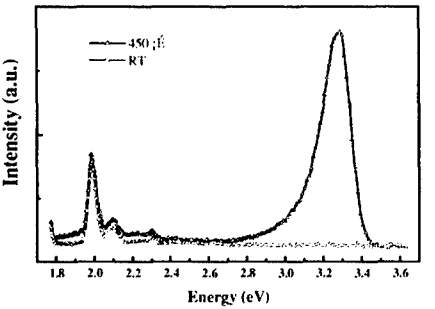


Figure 5. CL spectra of the ZnO films deposited at room temperature and 450 ℃

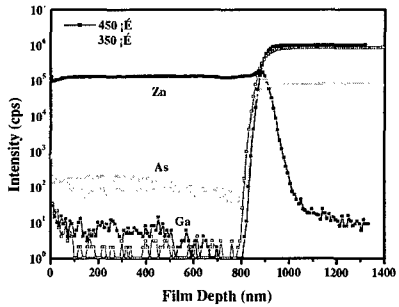


Figure 6. SIMS profiles of the ZnO films deposited at 350 ℃ and 450 ℃

uniformly distributed through the ZnO films, and the As atom concentration is a factor 10 higher than the Ga concentration. The SIMS results indicate that the As doping method using GaAs substrate might be useful for the formation of p-type ZnO thin films. However, all as-grown films showed electrically insulating properties with high contact resistance (>25 MΩ). Considering that the films exhibited the high resistvity, it is thought that the doped As atoms were not electrically activated due to insufficient activation energy.

In order to activate As dopants, post-annealing treatment at 500 ℃ was performed for the films deposited at 350 ℃ and 450 ℃. After 2-hr annealing treatment, the film deposited at 350 ℃ showed no change in electrical properties whereas the film deposited at 450 ℃ showed n-type characteristics with electron concentration of 3×10^{18} /cm^3 and resistivity of 9.65×10^{-2} Ω·cm.

However, a significant change of optical properties was observed after post-annealing treatment. Figure 7 shows the room-temperature PL spectra of ZnO films deposited at 350 ℃ and 450 ℃ after annealing treatment at 500 ℃. For the film deposited at 350 ℃, the intensity of NBE at 3.28 eV was much stronger than that of the as-grown films and this

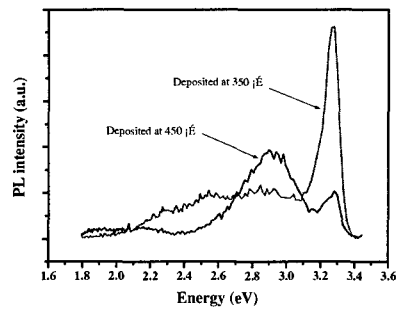


Figure 7. PL spectra of ZnO films deposited at 350 ℃ and 450 ℃ after annealing treatment at 500 ℃

indicates improvement in optical properties. For the film deposited at 450 ℃, however, the peak intensity related to the donor-to-acceptor pair (DAP) transition at 2.9 eV is increased. Therefore, it is thought that annealing treatment activate As dopants which act act as acceptors.

CONCLUSION

ZnO films were deposited on GaAs(100) substrates by rf magnetron sputtering. As deposition temperature increased, grain growth of the films was observed from SEM images. The results of XRD analysis showed the change of preferred orientations of the film growth and the relaxation of stress in the films with increasing deposition temperature. CL measurement showed that, for the films deposited at R.T., only defect-related deep-level emission was observed while, for the films deposited at 450 ℃, a strong NBE was observed, implying they are optically high-quality.

After annealing treatment for activating As dopants, the films deposited at 450 ℃ exhibited smaller resistivity than that of the as-grown films, although they showed n-type characteristics with 3×10^{18} /cm^3 of carrier concentration. In PL spectra of the films, DAP transition at 2.9 eV was dominant due to the activation of As dopants, which suggests the possibility of p-type doping of ZnO films when GaAs substrate is employed.

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